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Customer No. 000027683

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:
Guoxian Liang et al.

Serial No.: 10/770,939

Filed: February 3, 2004

For: Ca-Mm-Ni BASED HYDROGEN
STORAGE ALLOYS

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§
§ Confirmation No.: 1631
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§ Group Art Unit: 1742
§
§ Examiner: Unknown
§
§

TRANSMITTAL

Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Enclosed are the following regarding the above-identified patent application:

1. Claim of Priority under 35 U.S.C. § 119;
2. Certified copy of Canadian Patent Application No. 2,418,332;
3. This Transmittal in duplicate; and
4. A Return Postcard.

The Commissioner is hereby authorized to charge any further fees associated with this communication or to credit any overpayment to Deposit Account No. 08-1394.

Respectfully submitted,

Randall C. Brown
Registration No. 31,213

Dated: 11/1/04

HAYNES AND BOONE, LLP
901 Main Street, Suite 3100
Dallas, Texas 75202-3789
Direct Phone: (214) 651-5242
Facsimile: (214) 200-0853
File: 25000.16

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Ellen Lovelace



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CLAIM OF PRIORITY UNDER 35 U.S.C. § 119

Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Under the provisions of 35 U.S.C. § 119 Applicant hereby claims the priority of Canadian Application No. 2,418,332, filed February 4, 2003, which is mentioned in the declaration of the above-identified application. A certified copy of the Priority Document is submitted herewith.

The Commissioner is hereby authorized to charge any further fees associated with this communication or to credit any overpayment to Deposit Account No. 08-1394.

Respectfully submitted,

Randall C. Brown
Registration No. 31,213

Dated: 11/1/04

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Ellen Lovelace



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attached hereto and identified below are
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Specification and Drawings, as originally filed, with Application for Patent Serial No:
2,418,332, on February 4, 2003, by **HERA, HYDROGEN STORAGE SYSTEMS
INC.**, assignee of Guoxian Liang and Robert Schulz, for "Ca-Mm-Ni Based Hydrogen
Storage Alloys".

**CERTIFIED COPY OF
PRIORITY DOCUMENT**

Gracy Paulhus
Agent certificateur/Certifying Officer

August 10, 2004

Date

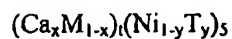
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ABSTRACT

New alloys of the AB₅ type are disclosed which are of the formula:



where M is one or several metals selected from the group consisting of misch metal (Mm) and other rare earth metals

T is one or several semi-metals such as Si, Ge and Ga;

$$0 < x \leq 1;$$

$$0 < y \leq 0.5 \text{ and}$$

$$0.8 \leq t \leq 1.2.$$

Also disclosed is a process for preparing these new alloys and their use for hydrogen storage.

Ca-Mm-Ni BASED HYDROGEN STORAGE ALLOYS**Field of the invention**

5

The present invention relates to new Ca-Mm-Ni based alloys of the AB₅ type.

The invention also relates to a process for preparing these new alloys and to the use of such new alloys for hydrogen storage.

10

Background of the invention

The use of hydrogen gas as a fuel for PEM fuel cells has received considerable attention in recent years in view of the fact that PEM fuel cells using pure hydrogen can provide
15 high efficiency and ultra clean power. Unfortunately, the widespread use of hydrogen energy is limited by economic and technological barriers. One of the important barriers is the lack of cost effective, safe hydrogen storage method.

Hydrogen gas is very light. It can be compressed under high pressure and stored in
20 pressurized vessels. It can also be liquefied and stored in liquid form. Hydrogen also reacts with metal or non-metals to form hydrides. Some metal hydrides are reversible at ambient temperature and pressures. From a safety point of view, metal hydrides are intrinsically safe since the hydrogen must be released from the hydrides by an endothermic process before it can burn or be oxidized.

25

The volumetric density of hydrogen storage in metal hydrides is usually high. The most serious shortcomings of the reversible low temperature metal hydrides are their low gravimetric storage density and their high cost. For stationary and some mobile applications, the weight of the hydrogen storage tank is not a problem. However, the
30 high cost of conventional low temperature metal hydrides results in too expensive storage devices.

CaNi₅ intermetallic compound represents a category of low cost hydrogen storage materials with a maximum storage capacity up to 1.9wt.% (see reference 1). However, little attention has been paid to this system, probably due to its well-known bad cycling stability (see reference 2). Improvement of the hydrogen storage properties of CaNi₅ by substitution of Ca or Ni with other elements has been tried (see references 3 to 5). Ternary Ca_xMm_{1-x}Ni₅ and quaternary Ca_xMm_{1-x}Ni_{5-y}Cu_y alloys have been produced by melt casting and patented 20 years ago (see reference 6). Substitution of Mm (mish metal) for Ca can raise the plateau pressure of CaNi₅. However, the plateau slope is big for the as-cast ternary alloys due to segregation. Annealing at elevated temperatures (>1000C) can reduce the slope to some extent. The inventor's previous work show that CaNi₅ and Mm and/or Zn-substituted CaNi₅ type alloys with flat plateau can be successfully produced (see reference 7).

Substitution of Ni by Mm and Al in the CaNi₅ type alloys can improve the cycling stability as disclosed in US 4,631,170 (see reference 8). However, the long term cycling stability of the alloys according to this patent is still not good enough. Typically more than 20% of the capacity is lost upon 200 times of hydrogen absorption/desorption cycling.

Further improvement has been achieved by concomitant substitution of Mm for Ca and Zn and Al for Ni, as reported by the present inventors of record (see reference 9). The capacity loss after 500 cycles has proved to be less than 20% for Ca_{0.8}Mm_{0.2}Ni_{4.8}Zn_{0.1}Al_{0.1} and less than 10% for Ca_{0.7}Mm_{0.3}Ni_{4.8}Al_{0.1}Zn_{0.1}. However, the maximum storage capacity is significantly reduced by substitution of Zn and Al for Ni.

25

Summary of the invention

In accordance with the present invention, it has now been found that substitution of Si, Ge and some other metalloid elements (also called "semi-metals") for Ni in a ternary Ca-Mm-Ni alloy of the AB₅ type can substantially improve the long term stability of such an alloy without causing much reduction of the storage capacity. Essentially, no capacity loss has been observed after 500 hydrogen absorption and desorption cycles.

30

Thus, a first object of the present invention is to provide new Ca-Mm-Ni based alloys of the AB₅ type, which are capable of absorbing and desorbing hydrogen from a gas phase at ambient temperature with a relative flat plateau pressure and a storage capacity larger
 5 than 1.2wt.%. These new alloys are of the formula (I):



where M is one or several metals selected from the group consisting of misch metal
 10 (Mm), Y and other rare earth metals;

T is one or several semi-metals such as Si, Ge and Ga;

$$0 < x \leq 1;$$

$$0 < y \leq 0.5 \text{ and}$$

$$0.8 \leq t \leq 1.2.$$

15

Another object of the invention is to provide a process for the preparation of the above mentioned alloys of formula (I), which comprises the following steps:

- a) preparing a powder by milling a mixture of elemental powders and/or pre-alloyed substances of the elemental ingredients of the alloy to be prepared (such as, for
 20 example, Ca, Ni, Mm, CaNi₂, CaNi₅, MmNi₅ and so on) in adequate proportions to obtain the required alloy; and
- b) annealing and/or sintering the so prepared powder at elevated temperatures in a crucible for a short period of time in an inert or reactive atmosphere.

25 In use, step a) may consist of a ball milling or of a mechanical alloying and can be carried out at room temperature or at high temperatures with or without anti-sticking agents.

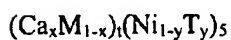
Step b) is essential to the above process. This step must actually be carried out to
 30 achieve high reversible capacity and a flat plateau. In use, the annealing can be carried in a crucible made of stainless steel at a temperature higher than 600°C but not higher than 1100°C.

Alternatively, the new compounds according to the invention can be produced by conventional melt casting methods or powder sintering methods.

- 5 The compounds according to the invention are useful for hydrogen storage in a gaseous form and such is a further object of the invention.

DETAILED DESCRIPTION OF THE INVENTION

- 10 As aforesaid, the invention is directed to new alloys of the AB_5 type, which are of the formula:



- 15 where M is one or several metals selected from the group consisting of misch metal Mm, Y and other rare earth metals
 T is one or several semi-metals such as Si, Ge and Ga;
 $0 < x \leq 1$ ($x \neq 0$), preferably $0.4 \leq x \leq 1$;
 $0 < y \leq 0.5$ ($y \neq 0$), preferably $0 < y \leq 0.3$; and
 20 $0.8 \leq t \leq 1.2$.

- As aforesaid, the invention is actually based on the discovery that significant further improvements have been achieved by substituting Si, Ge and/or other semi-metals for Ni in the above mentioned Ca-Mm-Ni alloy of the AB_5 type (see the definition of T in
 25 the formula given hereinabove). This substitution has significant effect of improving the long-term stability while keeping predominantly the AB_5 structure and hydrogen storage capacity according to the invention that are particularly useful.

- The new Ca-Mm-Ni alloys of the AB_5 type according to the invention with improved
 30 properties can be made by mechanical alloying of elemental powders (such as Ca, Mm, Ni_5) and/or mixtures of intermetallic compounds (such as $CaNi_5$, $MmNi_5$) corresponding to the required composition, followed by an thermal annealing treatment at temperatures

higher than 600°C for short period of time, typically at 1000°C or slightly higher for 0.5h-1h in a steel crucible. Annealing at temperatures lower than 600C does not improve the hydrogen storage properties very much.

- 5 The invention and its advantages will be better understood upon reading the following description made with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

- 10 Fig. 1 is a curve giving the hydrogen storage capacity of an alloy of formula $(\text{Ca}_{0.64} \text{Mm}_{0.36})_{1.1} \text{Ni}_5$ as a function of the pressure after 3 cycles and 250 cycles;

Fig. 2 is a curve similar to the one of Fig. 1, but with an alloy of formula $(\text{Ca}_{0.64} \text{Mm}_{0.36})_{1.1} \text{Ni}_{4.9} \text{Si}_{0.1}$;

15

Fig. 3 is a curve similar to the one of Fig. 1, but with an alloy of formula $(\text{Ca}_{0.64} \text{Mm}_{0.36})_{1.1} \text{Ni}_{4.8} \text{Si}_{0.2}$;

- 20 Fig. 4a is a X-ray analysis of the alloy of formula $(\text{Ca}_{0.64} \text{Mm}_{0.36})_{1.1} \text{Ni}_{4.8} \text{Si}_{0.2}$ mentioned hereinabove (see Fig. 3);

Fig. 4b is an X-ray analysis of the alloy of formula $(\text{Ca}_{0.64} \text{Mm}_{0.36})_{1.1} \text{Ni}_5$ mentioned hereinabove (see Fig. 1); and

- 25 Fig. 5 is a curve similar to the one of Fig. 1, but with an alloy of formula $(\text{Ca}_{0.64} \text{Mm}_{0.36})_{1.1} \text{Ni}_{4.85} \text{Ge}_{0.15}$.

EXAMPLE 1 (Preparation of a known compound by the process of the invention)

- 30 $(\text{Ca}_{0.64} \text{Mm}_{0.36})_{1.1} \text{Ni}_5$ was synthesized by mechanical alloys in a SPEX high energy ball mill under argon. A MmNi_5 powder (>99%, + 100mesh), Ca granules (>99.5, ~2mm in size) and Ni powders (<99.9%, -325mesh) were used as starting materials.

After alloying, an isothermal annealing was performed in a tubular furnace under argon. The mechanically alloyed powder was sealed in a stainless steel crucible before annealing. The powder was heated to 1050°C at a heating rate of 30C/min, and held at 1050°C for 1 hour, then cooled down to room temperature in the furnace.

5

The hydrogen absorption/desorption properties were measured by using an automatic Sievert's type apparatus. The annealed powder normally needs mild activation treatment, such as heated to 200°C under vacuum and then cooled down. The activated $(\text{Ca}_{0.64}\text{Mm}_{0.36})_{1.1}\text{Ni}_5$ alloy exhibits a relative flat plateau and a maximum storage capacity of 1.44 wt.% under 4.0MPa of charging pressure.

10

A hydrogen absorption/desorption cycling experiment was performed at 30°C under an absorption pressure of 3.5MPa and a desorption pressure of 0.01MPa. The absorption and desorption time was 12 minutes respectively. Under these conditions, the alloys could be fully hydrided and dehydrided. The hydrogen purity was 99.999%. As shown in Fig. 1, the maximum storage capacity was reduced to 1.23 wt.% after 250 cycles (20% loss). The reduction of the effective reversible storage capacity is even bigger.

15

EXAMPLE 2 (Compound according to the invention made by the process of the invention)

20

$(\text{Ca}_{0.64}\text{Mm}_{0.36})_{1.1}\text{Ni}_{4.9}\text{Si}_{0.1}$ was synthesized by mechanical alloying of elemental Ca, Si and MmNi₅ powder blends. The alloy was annealed in the same manner as in Example 1. This alloy had a maximum hydrogen storage capacity of 1.4wt.%. The maximum hydrogen storage capacity are slightly reduced by 8% after 250 cycles as shown in Fig.2 in contrast to the 20% loss in the $(\text{Ca}_{0.64}\text{Mm}_{0.36})_{1.1}\text{Ni}_5$.

25

EXAMPLE 3 (Compound according to the invention made by the process of the invention)

30

$(\text{Ca}_{0.64}\text{Mm}_{0.36})_{1.1}\text{Ni}_{4.8}\text{Si}_{0.2}$ was synthesized by mechanical alloying of elemental Ca, Si and MmNi₅ powder blends. The alloy was annealed in the same manner as in Example

($\text{Ca}_{0.64}\text{Mm}_{0.36}$) $_{1.1}\text{Ni}_{4.8}\text{Si}_{0.2}$ was synthesized by mechanical alloying of elemental Ca, Si and MmNi₅ powder blends. The alloy was annealed in the same manner as in Example 1. This alloy had a hydrogen storage capacity of 1.3wt.%. The maximum and reversible hydrogen storage capacities are slightly improved upon hydrogen absorption and desorption cycling as shown in Fig.3.

X-ray analyses show that Si-substituted alloys have very high resistance to peak broadening upon cycling as shown in Fig.4a. While the ($\text{Ca}_{0.64}\text{Mm}_{0.36}$) $_{1.1}\text{Ni}_5$ alloy without Si substitution shows obvious peak broadening after cycling as shown in Fig. 4b. It was believed that hydrogen absorption/desorption cycling introduces defects, such as microstrain, chemical disorders and grain boundaries (reduced grain size), therefore leads to reduced storage capacity. The peak broadening reflects the defects introduced during cycling experiments.

EXAMPLE 4 (Compound according to the invention made by the process of the invention)

$\text{Ca}_{0.7}\text{Mm}_{0.4}\text{Ni}_{4.85}\text{Ge}_{0.15}$ was synthesized by mechanical alloying of elemental powder blends. The alloy was annealed in the same manner as in Example 1. This alloy had a maximum hydrogen storage capacity of 1.3wt.% in the as-synthesized state. Substantial improvement in the maximum and reversibly storage capacity is observed after 500 cycles as shown in Fig.5.

REFERENCES

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- (2) "Stability of Rechargeable hydriding alloys during extended cycling" by P. D. Goodell, J Less-Common Met., 99 (1984) 1.
- 10 (3) "Systematic B-metal substitution in CaNi₅" by J.O. Jensen and N.J. Bjerrum: J. of Alloys and Compounds 293-295 (1999) 185
- (4) "Hydriding behavior in Ca-Mg-Ni-B" by H. Oesterreicher, K. Ensslen, A. Kerlin and E. Bucher": Mat. Res. Bull. 15 (1980) 275.
- (5) "Mechanical alloying and hydrogen storage properties of CaNi₅-based alloys", by G. Liang, J. Huot and R. Schulz, J. Alloys & Compounds, 321
- 15 (2001) 146.
- (6) "Nickel-misch metal-Calcium alloys for hydrogen storage" by G.D. Sandrock, US patent Nos. 4,096,639 and 4,161,402.
- (7) "Synthesis of nanocrystalline CaNi₅-based alloys and use for metal hydride electrode", by G. Liang, S. Ruggeri, C. Lenain, H. Alamdari, J. Huot, L.
- 20 Roue and R. Schulz", J. Metastable and Nanocrystalline Materials 11 (2001) 71.
- (8) "Calcium-Nickel-misch metal-Aluminium quaternary alloy for hydrogen storage", by K. Ohnishi, T. Ogawa, US patent, 4631170.
- (9) "Synthesis of low cost metal hydrides by mechanical alloying" by G. Liang
- 25 and R. Schulz, Report for the CRADA project (CR-99-004), 2001.

CLAIMS

1. A Ca-Mm-Ni based alloy of the AB₅ type, said alloy being of the formula:

5



where M is one or several metals selected from the group consisting of misch metal Mm, Y and other rare earth metals;

10 T is one or several semi-metals such as Si, Ge and Ga;

$$0 < x \leq 1;$$

$$0 < y \leq 0.5; \text{ and}$$

$$0.8 \leq t \leq 1.2.$$

15 2. The alloy of claim 1, wherein, in the formula I:

$$0.4 \leq x \leq 1;$$

$$0 < y \leq 0.3; \text{ and}$$

$$0.8 \leq t \leq 1.2$$

20 3. The alloy of claim 1 or 2, wherein:

M is a misch metal; and

T is selected from the group consisting of Si, Ge and Ga.

4. Use of the alloy of claim 1, 2 or 3 for storing hydrogen.

25

5. A process for the preparation of an alloy of formula (I) as defined in claim 1, 2 or 3, comprising:

a) preparing a powder by milling a mixture of elemental powders and/or pre-alloyed substances of the elemental ingredients of the alloy to be prepared in adequate proportions to obtain the required alloy; and

30

b) annealing and/or sintering the so prepared powder at elevated temperatures in a crucible for a short period of time in an inert or reactive atmosphere.

6. The process of claim 5, wherein the milling step (a) consists of a ball milling or mechanical alloying.
- 5 7. The process of claim 6, wherein the milling step (a) is carried out in the presence of at least one anti-sticking agent.
8. The process of any one of claims 5 to 7, wherein the annealing and/or sintering step (b) is carried out at a temperature higher than 600°C but not higher than 1100°C in a
- 10 steel crucible.

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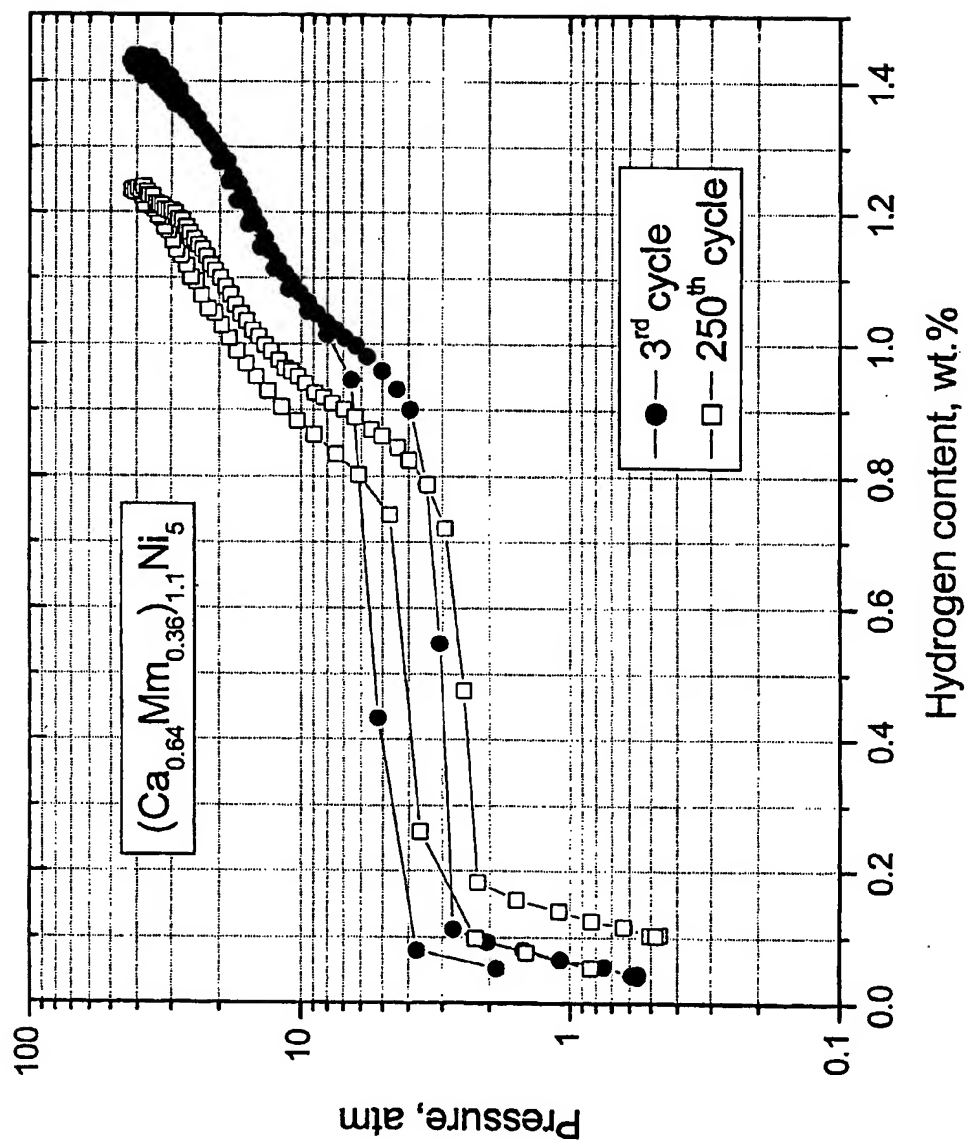


FIG. 1

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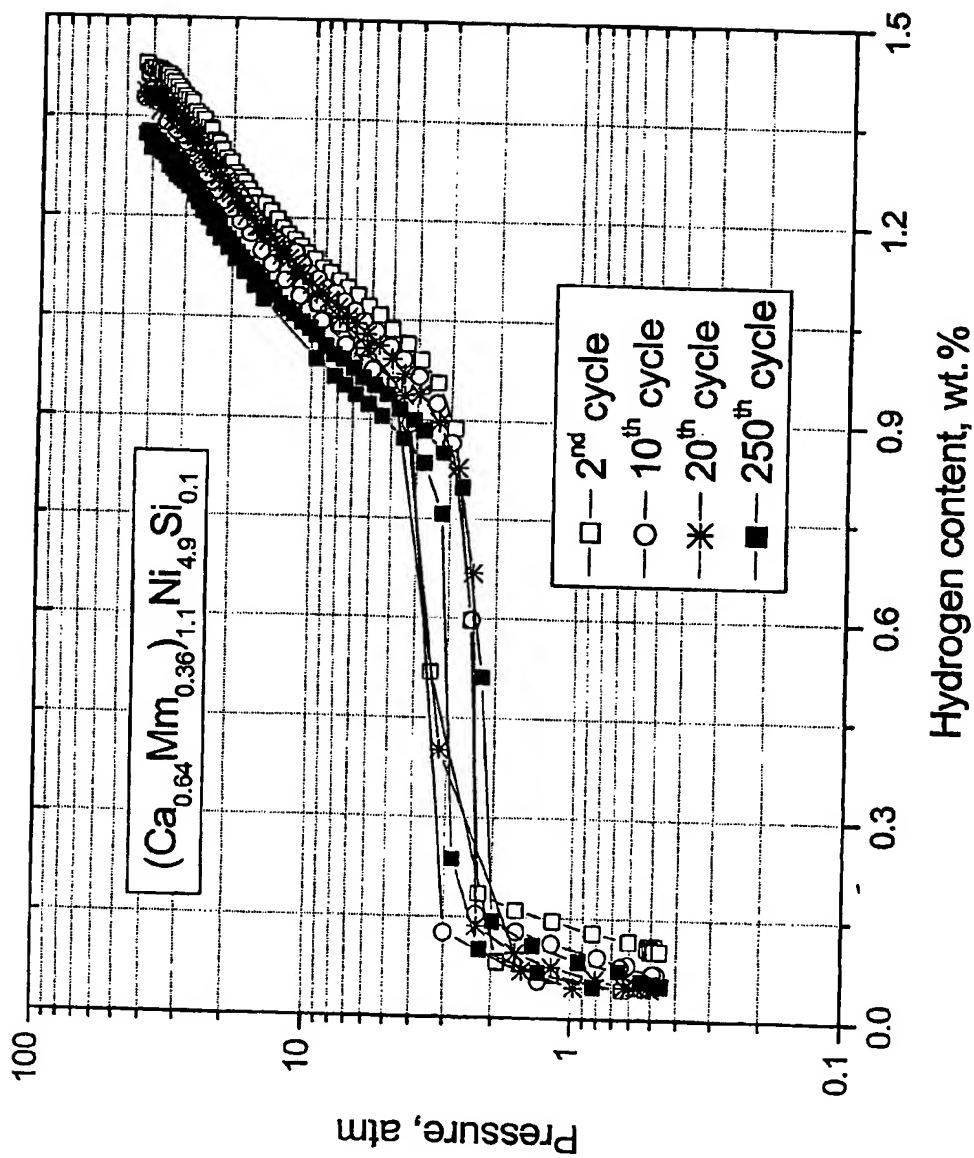


FIG. 2

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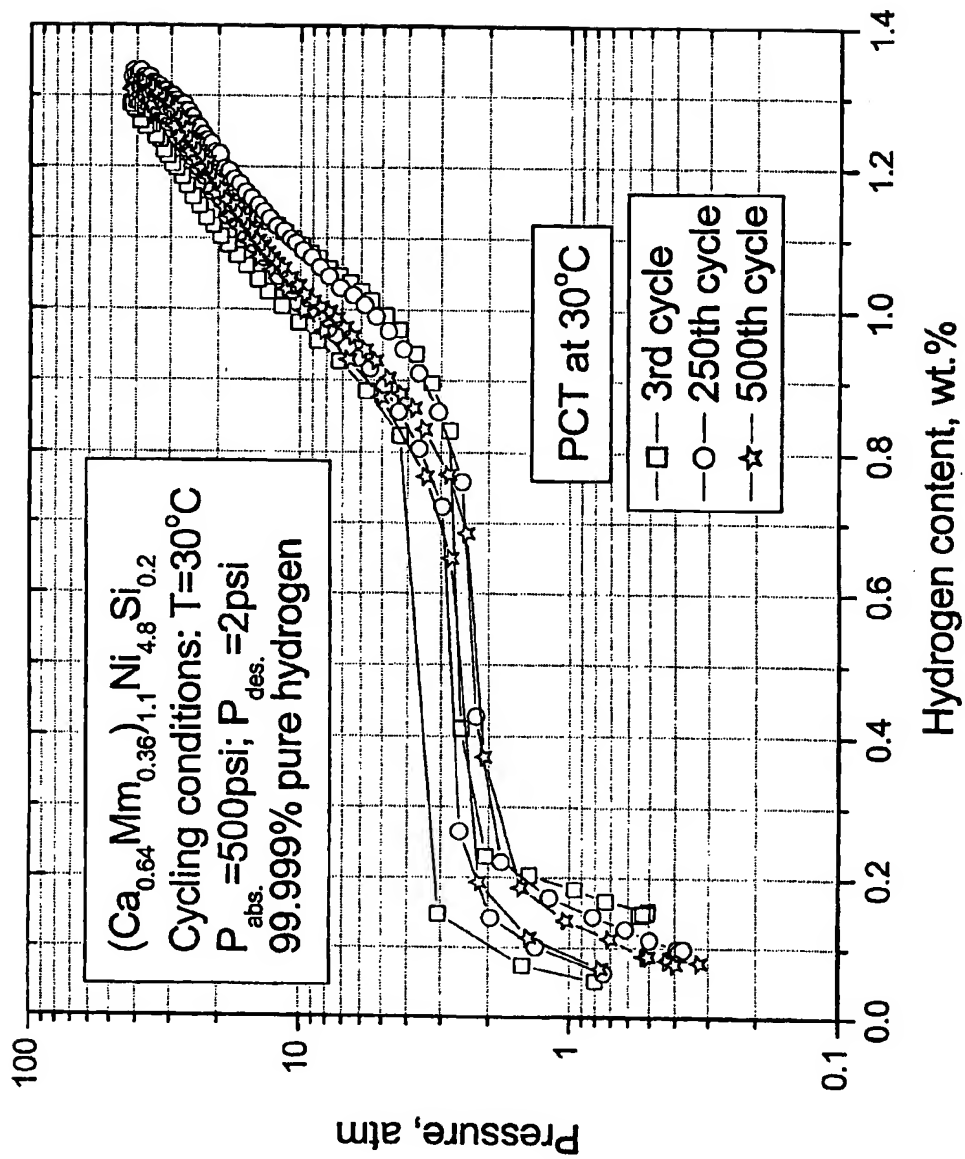
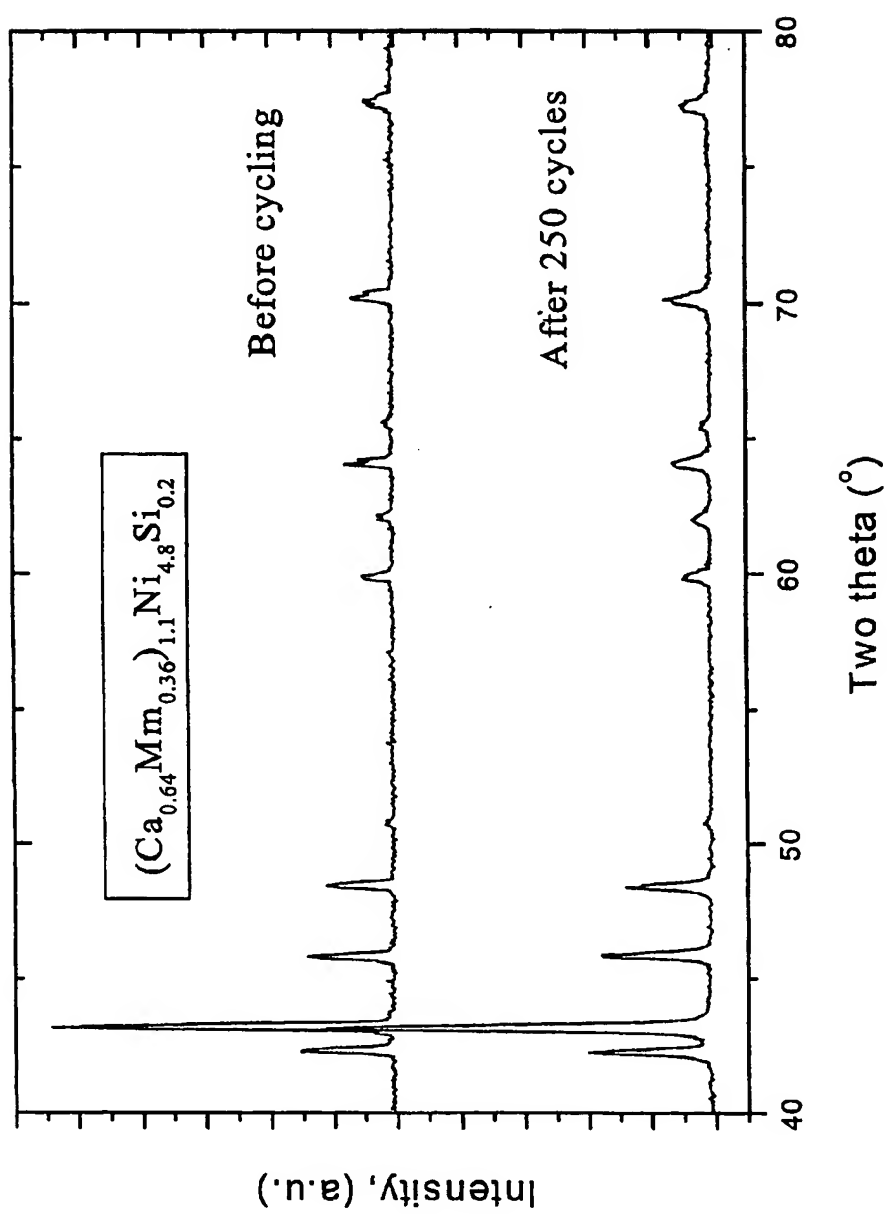


FIG. 3

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FIG. 4a

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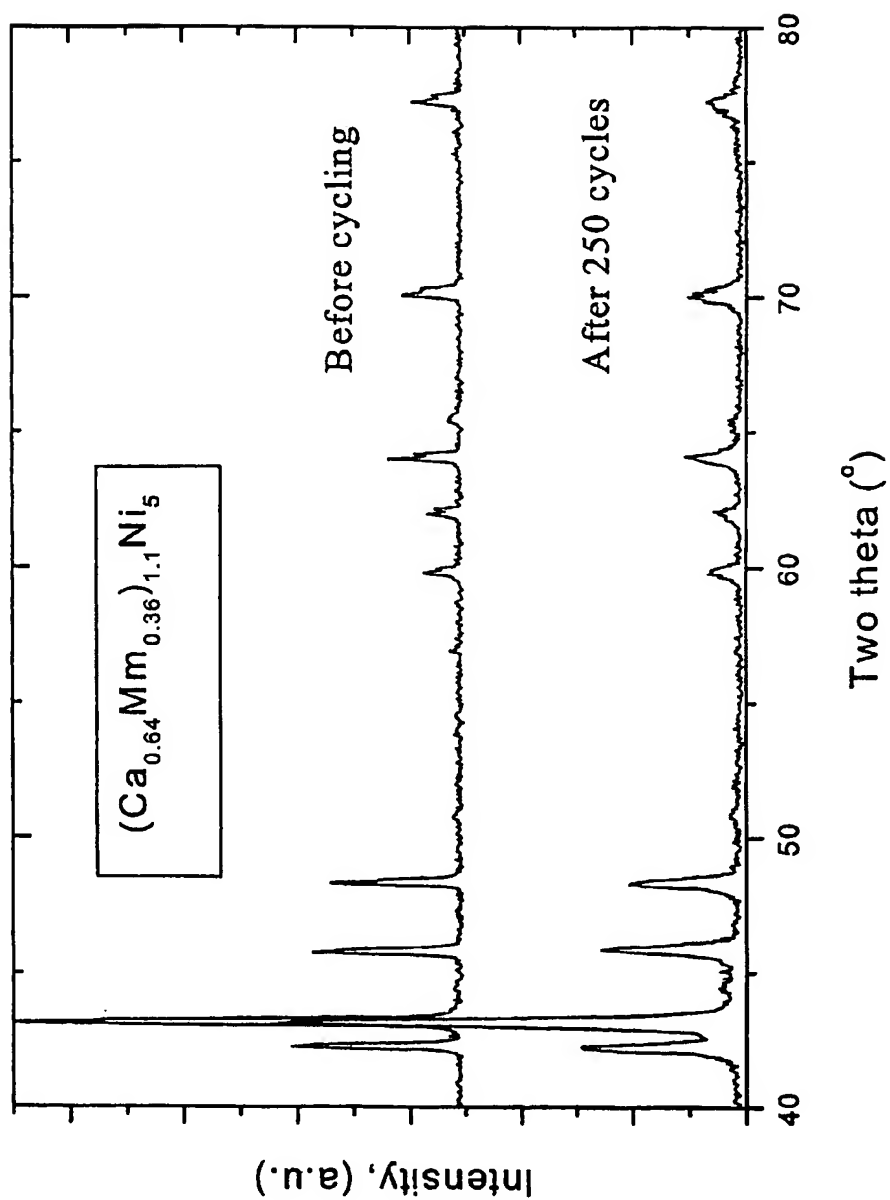


FIG. 4 b

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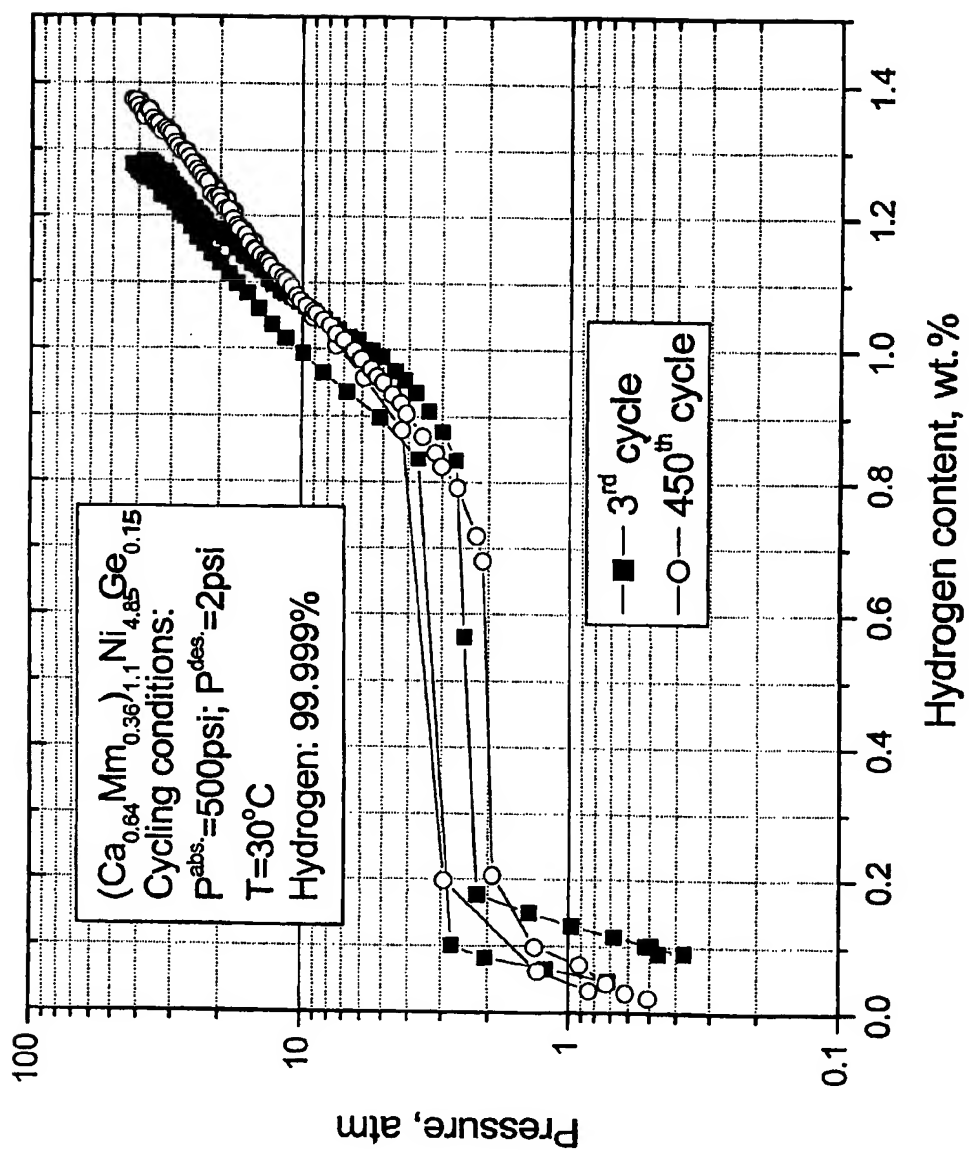


FIG. 5